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AN EVALUATION OF CORROSION PROTECTION BY TWO EPOXY PRIMERS ON 2219-T87 AND 7075-T73 ALUMINUM

By M.J. Mendrek

Materials and Processes Laboratory Science and Engineering Directorate

October 1992



George C. Marshall Space Flight Center

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13. ABSTRACT (Maximum 200 words) A comparison of the corrosion protection provided by two amine epoxy primers was made using salt fog, alternate immersion, and total immersion as exposure media. The study is the result of a request to use an unqualified low volatile organic carbon (VOC) primer (AKZO 463-6-78) in place of the current primer (AKZO 463-6-3) because environmental regulations have eliminated use of the current primer in many states. Primed, scribed samples of 2219-T87 and 7075-T73 aluminum were exposed to 5-percent NaCl salt fog and 3.5-percent NaCl alternate immersion for a period of 90 days. In addition, electrode samples immersed in 3.5-percent NaCl were tested using electrochemical impedance spectroscopy (EIS). The EG&G model 368 ac impedance measurement system was used to monitor changing properties of AKZO 463-6-78 and AKZO 463-6-3 primed 2219-T87 aluminum for a period of 30 days. The response of the corroding system to a frequency scan can be modeled in terms of an equivalent circuit consisting of resistors and capacitors in a specific arrangement. Each resistor/capacitor combination represents physical processes taking place within the electrolyte, at the electrolyte/primer surface, within the coating, and at the coating/substrate surface. Values for the resistors and capacitors are assigned following a nonlinear least squares fit of the data to the equivalent circuit. Changes in the values of equivalent circuit parameters during the 30-day exposure allow assessment of the time to and mechanism of coating breakdown.			
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TECHNICAL MEMORANDUM

AN EVALUATION OF CORROSION PROTECTION BY TWO EPOXY PRIMERS ON 2219-587 AND 7075-T73 ALUMINUM

INTRODUCTION

As a result of recent legislation restricting the use of high volatile organic content (VOC) paints, the solid rocket booster (SRB) contractor, United Space Boosters, Inc. (USBI), has proposed changing primers on certain aluminum hardware. The proposed primer, AKZO 463-6-78, is an amine epoxy with strontium chromate added as a corrosion preventative, and has a VOC of 337 grams/liter. The current primer, AKZO 463-6-3 is also an amine epoxy, but utilizes calcium and lead chromates as corrosion preventatives and has a VOC of 650 grams/liter.

In response to USBI's request to use the AKZO 463-6-78 primer, a test program comparing the two primers was initiated. This program included (1) conventional testing of coated, scribed panels in salt fog and alternate immersion, (2) standard wet tape adhesion testing, and (3) a 30-day comparison using the electrochemical alternating current (ac) impedance technique. The impedance testing was included as part of the general development of this technique in evaluating coated samples. A brief description of this technique follows. However, for a more detailed review of the ac impedance method, the reader is referred to three papers (refs. 1, 2, and 3) which should prove beneficial in understanding this technique.

EQUIVALENT CIRCUITS

The basis of the ac impedance method is the modeling of the corrosion cell in terms of a purely electronic circuit. A suitable equivalent circuit should reasonably reproduce experimental plots obtained from the corrosion cell when experimentally determined parameters are used. These plots include Bode magnitude (impedance versus log w, where $2 = 2\pi \times$ frequency), Bode phase, and complex plane or Nyquist plot (-Z" versus Z'). Previous investigations (refs. 1 and 2) have demonstrated that the equivalent circuit shown in figure 1 best represents the ac impedance response of a corroding bare metal surface. Equivalent circuits for coated metal surfaces, however, are more complex, requiring additional resistor/capacitor combinations. The equivalent circuit in figure 2 has been used previously to represent the response of primer coated 2219-T87 aluminum.³ It has also been used in the evaluation of primed and topcoated 4130 steel.⁴ The physical model this circuit represents is shown in figure 3.

ALTERNATING CURRENT DATA ANALYSIS

The goals of analyzing ac impedance data are threefold: (1) determine the equivalent circuit that most accurately describes the corrosion cell, (2) assign the best possible values to resistors

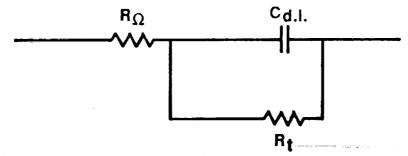
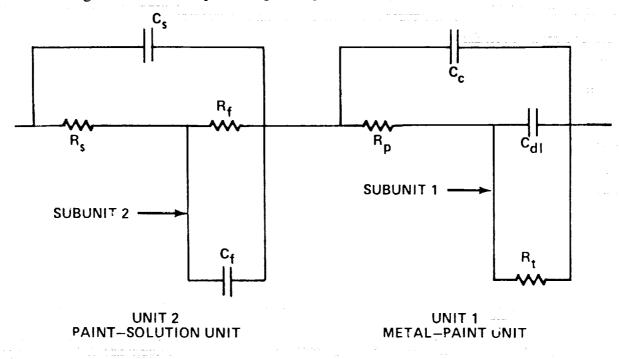


Figure 1. Circuit representing ac impedance response for bare metals.



$c_{\mathbf{S}}$	SOLUTION CAPACITANCE
$R_{\mathbf{S}}$	SOLUTION RESISTANCE
C _S R _S C _f	FARADAIC CAPACITANCE (COATING/SOLUTION)
R_f	FARADAIC RESISTANCE
C _c	COATING CAPACITANCE
R_{p}	COATING RESISTANCE
C _c R _p C _{d1}	METAL/COATING INTERFACE CAPACITANCE
Rt	CHARGE TRANSFER RESISTANCE

Figure 2. Circuit representing ac impedance response for primer coated 2219-T87 aluminum.

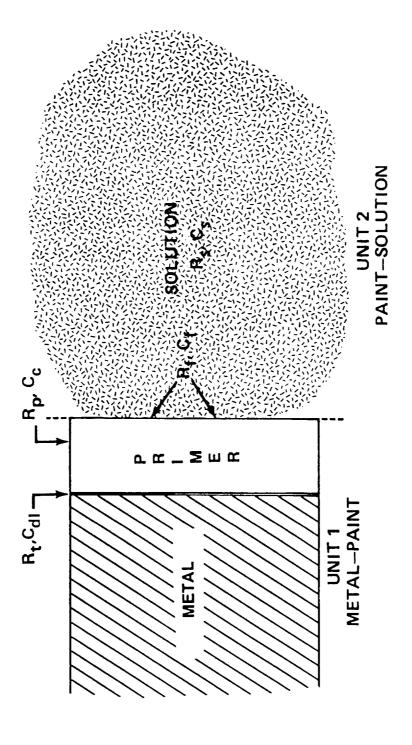


Figure 3. Physical description of circuit parameters for primer coated steel.

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and capacitors in the equivalent circuit for that particular experiment (impedance scans are generally performed every 2 days for 1 month), and (3) estimate the corrosion rate using equivalent circuit parameters. During sample immersion, model parameters will change in response to coating deterioration.

Reference 3 outlines the method of obtaining starting parameters from experimental Nyquist plots. These values are read into a complex least-squares program, which is based on an adaptation of the general nonlinear least-squares program ORGLS.⁴ It gives the best values for the parameters in the equivalent circuit. The quality of fit of the Bode magnitude data (Log |Z| versus Log w) for the primer coated systems tested is shown in figures 4 and 5. Both systems are described by the model in figure 2, with completely different parameters being required to fit the data.

The utility of the ac impedance technique, therefore, lies in the ability to obtain quantitative information on coatings performance. By assigning values to equivalent circuit parameters and tracking these parameters with time, it is possible to assess the mechanism of coating failure. Conventional coating evaluations are limited by the fact that they are qualitative in nature and that any speculation as to failure mechanism can only be made after test completion.

EXPERIMENTAL

This investigation was divided into two parts: conventional and electrochemical. The conventional testing involved exposing scribed, coated samples to 3.5-percent NaCl alternate immersion and 5-percent NaCl salt fog for a period of 90 days. Panels, 10.16 cm by 15.24 cm, (4 by 6 in) of 2219-T87 and 7075-T73 aluminum were alkaline etched, deoxidized, Iridite conversion coated, primed with AKZO 463-6-3 and AKZO 463-6-78 primers, then cured to manufacturers specifications. Primer thicknesses varied, but were in the range of 1.0 to 2.0 mils. Duplicate samples for each combination of alloy, environment, and primer were then marked with two diagonal scribes (exposing the bare aluminum), and placed in alternate immersion and salt fog. In addition, wet tape adhesion tests were performed. Single samples for each alloy and primer were prepared as previously discussed. Unscribed panels were immersed in deionized water for 24 h, removed, dried, and marked with a standard chevron scribe, exposing bare aluminum. 3M-250 tape, 2.54-cm (1.0-in) wide, was applied over the scribed area and pressed firmly to the surface with a blunt nonmetallic instrument. After 60 s, the tape was removed in one abrupt motion away from the panel.

Electrochemical test specimens, 1.587 cm (0.625 in) in diameter and 0.163 cm (0.064 in) thick, were prepared in the same manner as the conventional test panels, with a primer thickness of 1.2 mils, and immersed in a 3.5-percent NaCl solution for the entire test period. The sample holder, which exposes a sample with an area of 1.0 cm² to the test solution, is shown in figure 6. Testing was limited to a comparison of the primers on 2219-T87 aluminum. This alloy was chosen due to its low resistance to general corrosion compared to 7075-T73 aluminum. Measurements of ac impedance were made on alternate days for 1 month. Direct current measurements were not possible during this period because the currents generated in response to dc polarization are small with respect to the resolution of the instrumentation. Samples remained in the test solution for a total of 97 days, with additional measurements being made at 70 and 96 days on the 463-6-3 primer and at 71 and 97 days on the 463-6-78 primer. Deterioration of the 463-6-78 primer made it possible to use the direct current (dc) polarization resistance technique in addition to ac impedance on days 71 and 97.

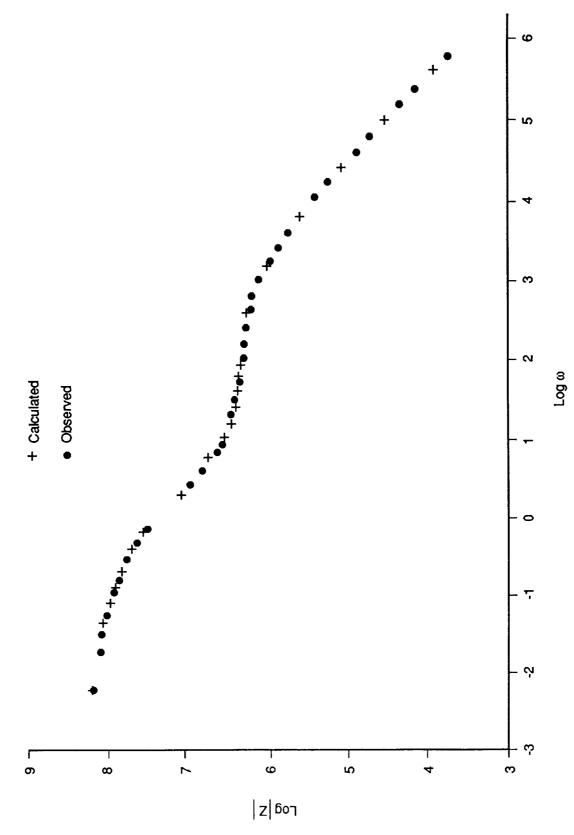


Figure 4. Least squares fit of Bode magnitude data-AKZO 463-6-3 primer coated 2219-T87 aluminum after 5 days in 3.5 percent NaCl.

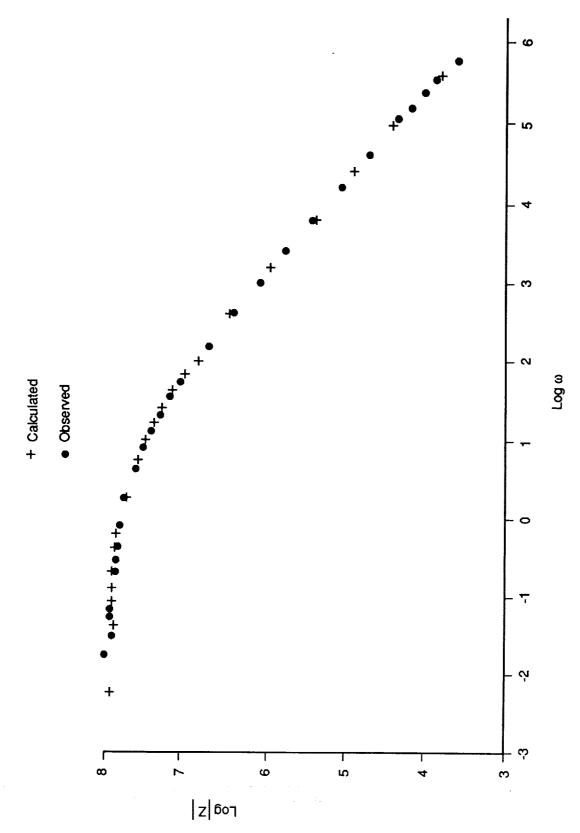


Figure 5. Least squares fit of Bode magnitude data-AKZO 463-6-78 primer coated 2219-T87 aluminum after 4 days in 3.5 percent NaCl.

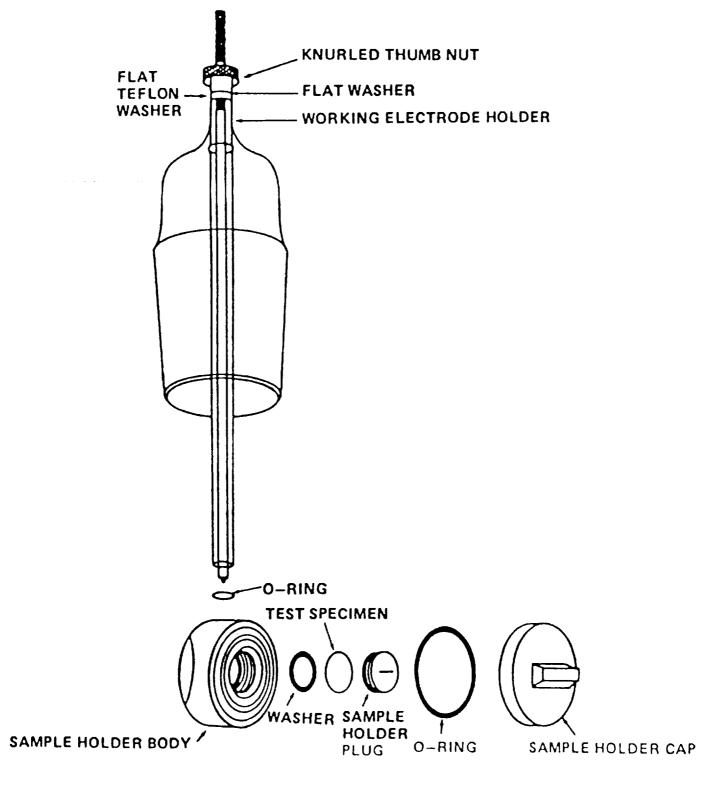


Figure 6. Exploded view of sample holder.

The EG&G PARC Model 368 ac impedance system was used for both ac impedance and dc polarization resistance data collection. Alternating current impedance data were taken in three sections. The first two sections, beginning at 0.001 Hz and 0.1 Hz respectively, were obtained using the fast Fourier transform (FFT) technique. The last section, ranging from 10 Hz to 100,000 Hz, was collected using the lock-in amplifier. The sequencing was performed automatically using the auto execute procedure, with all data for a given run being merged to a single set. The period of collection of the ac impedance data was about 2.5 h. After collection, the data were processed and analyzed as described in reference 3 using the equivalent circuit model of figure 2.

Data for the polarization resistance method were collected using the same system with the EG&G PARC model 332 corrosion measurement software, which was developed especially for dc measurements. The data were automatically corrected during the scan for IR drop using the technique developed by EG&G PARC. Data analysis was completed using the program POLCURR.⁶ The theory for the polarization resistance technique has been described previously.⁷

RESULTS AND DISCUSSION

Conventional Testing - Salt Fog and Alternate Immersion

Primed panels of 2219-T87 and 7075-T73 aluminum, after 90 days exposure to 3.5-percent NaCl alternate immersion and 5-percent NaCl salt fog, are shown in figures 7 through 14. Figures 7 and 8 compare the performance of the two primers on 7075-T73 aluminum in 3.5-percent alternate immersion. Comparison of the primers' performance on the remaining alloy/environment combinations are shown in figures 9 and 10, 11 and 12, and 13 and 14.

Results of these tests showed little difference between the two primers in the coated area. No blistering or peeling was noted on any panel, except adjacent to the scribe. However, the application for this primer system involves splashdown and retrieval of hardware, during which thermal insulation and coating materials may be stripped from the hardware. Therefore, an effective primer should not only be resistant to salt water, but should also provide protection to the base metal if the coating system is compromised. The diagonal marks scribed into the panels provide a convenient method of evaluating primer inhibitors. Optical inspection of scribe marks are summarized in the table below. Worst case pitting for each primer/alloy/environment combination is shown in figures 15 through 18.

7075-T73 ALUMINUM

AKZO 463-6-3 Primer

AKZO 463-6-78 Primer

3.5-Percent NaCl Alternate Immersion

Moderate pitting in scribe, several small pits extend into paint.

Slight pitting in scribe, only one pit extending into paint.

5-Percent Salt Fog

Extensive pitting in scribe, 10 pits extending into paint, 3 large pits extending into both sides of paint.

No pitting, only slight discoloration in scribe.

2219-T87 ALUMINUM

AKZO 463-6-3 Primer

AKZO 463-6-78 Primer

3.5-Percent NaCl Alternate Immersion

Slight pitting and discoloration in scribe, one pit extending into paint.

Slight pitting in scribe, one small pit extending into paint.

5-Percent Salt Fog

Moderate pitting in scribes, 11 pits extending into paint.

Discoloration and very slight pitting in scribe, one large pit extending into paint.

NOTE: Number of pits is the total of duplicate panels.

These results indicate only a slight difference in primer performance in 3.5-percent NaCl alternate immersion, favoring the 463-6-78 primer. This small difference is explained by the high resistance of both primers to degradation in this environment due to the effectiveness of inhibitor salts in the paint protecting the metal during immersion.

Results from the 5-percent salt fog testing, however, show conclusively the superiority of the AKZO 463-6-78 primer inhibitor additions. Only slight pitting in the scribe and a single pit extending into the primer were observed on the aluminum alloys coated with the 463-6-78 primer. However, extensive pitting in the scribe and undercut into the primer was observed for both aluminum alloys coated with the 463-6-3 primer. This does not allow the conclusion that the 463-6-78 primer is superior to the 463-6-3 primer, only that the inhibitors in the former provide better protection to adjacent bare metal than those in the latter.

Primer performance is based both on inhibitor effectiveness and on moisture resistance. Primers with low moisture resistance will blister, resulting in corrosion of the base metal, even if they contain an exceptional inhibitor system. Conversely, primers with excellent moisture resistance will eventually fail due to corrosion of the base metal if an effective inhibitor system is not



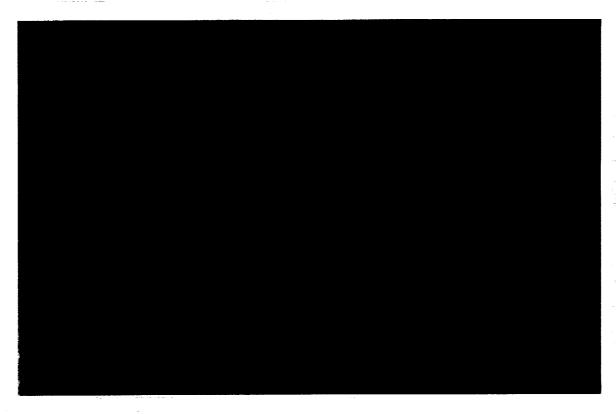
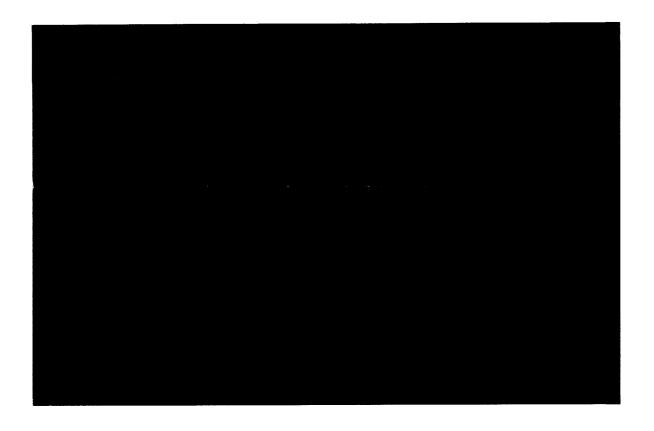


Figure 7. AKZO 463-6-3 primer on 7075-T73 aluminum after 90 days exposure to 3.5-percent NaCl alternate immersion.



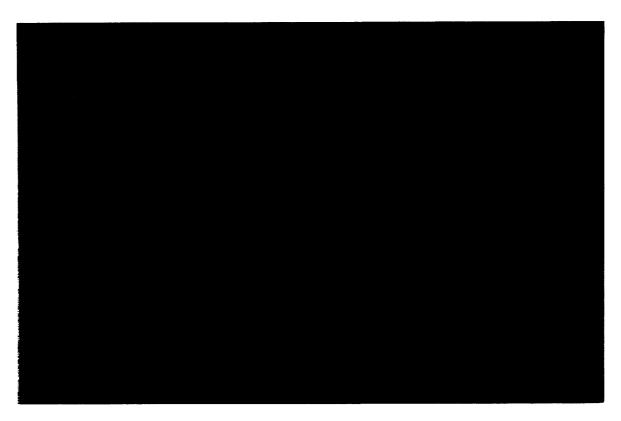
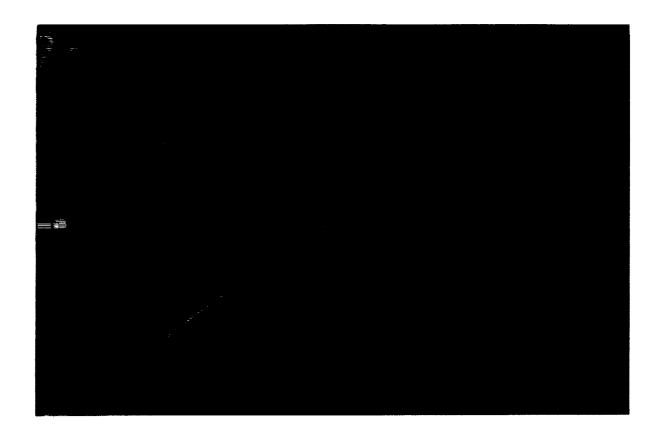


Figure 8. AKZO 463-6-78 primer on 7075-T73 aluminum after 90 days exposure to 3.5-percent NaCl alternate immersion.



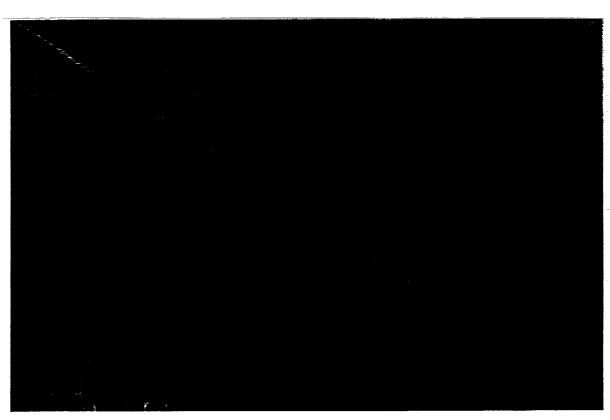


Figure 9. AKZO 463-6-3 primer on 7075-T73 aluminum after 90 days exposure to 5-percent NaCl salt fog.

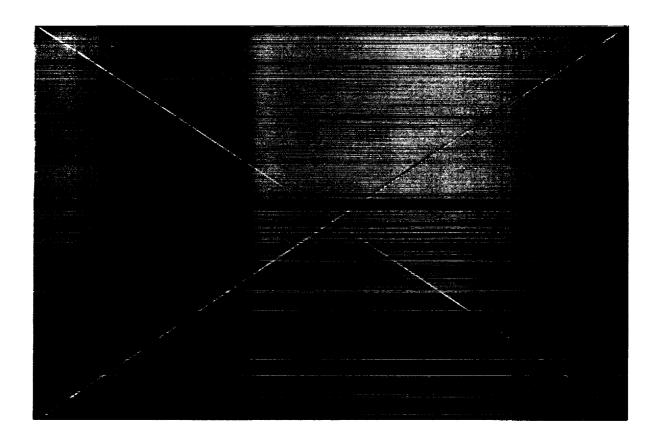
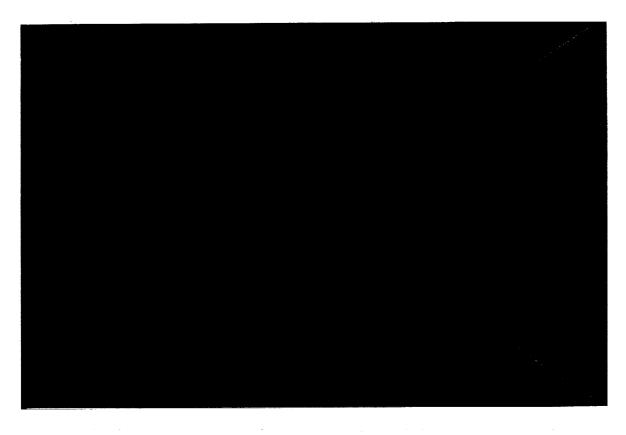




Figure 10. AKZO 463-6-78 primer on 7075-T73 aluminum after 90 days exposure to 5-percent NaCl salt fog.



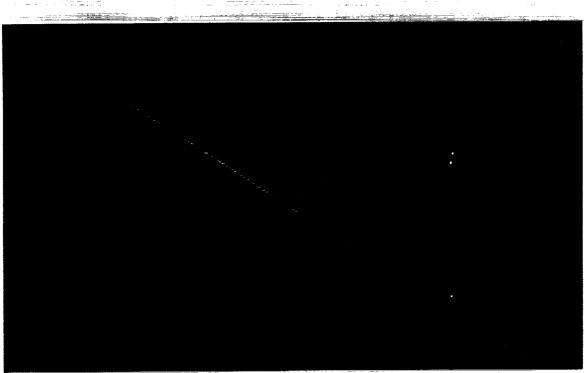
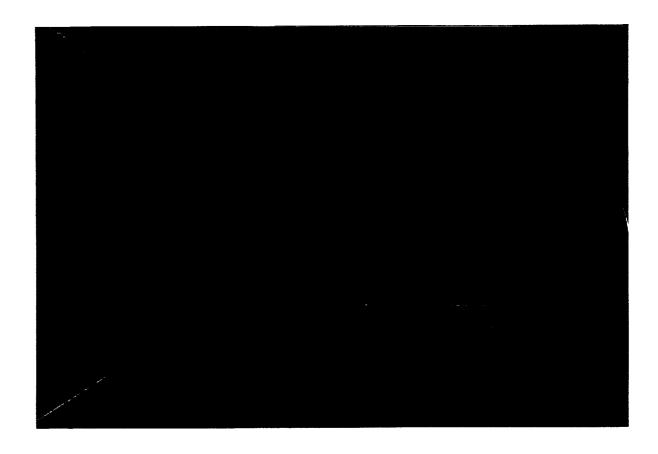


Figure 11. AKZO 463-6-3 primer on 2219-T87 aluminum after 90 days exposure to 3.5-percent NaCl alternate immersion.



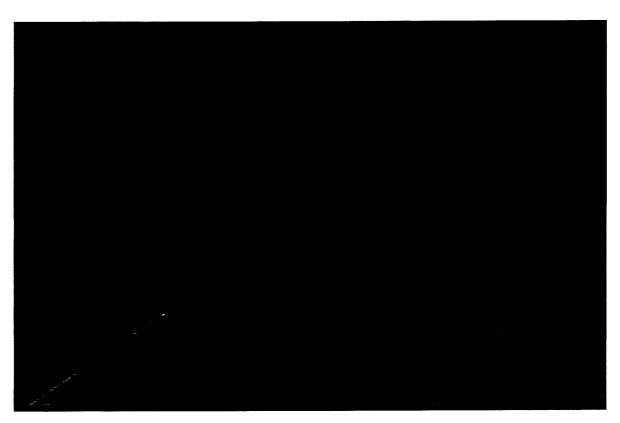
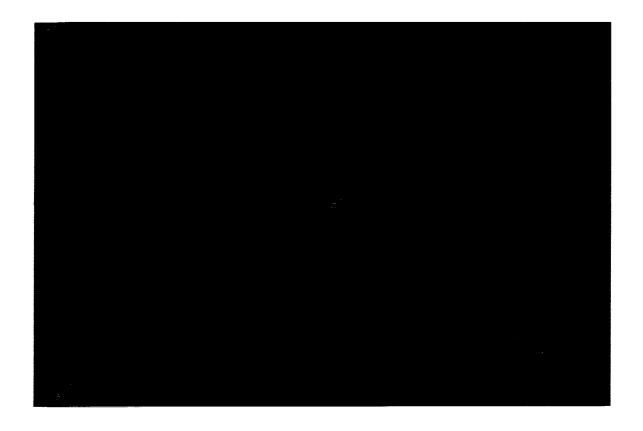


Figure 12. AKZO 463-6-78 primer on 2219-T87 aluminum after 90 days exposure to 3.5-percent NaCl alternate immersion.



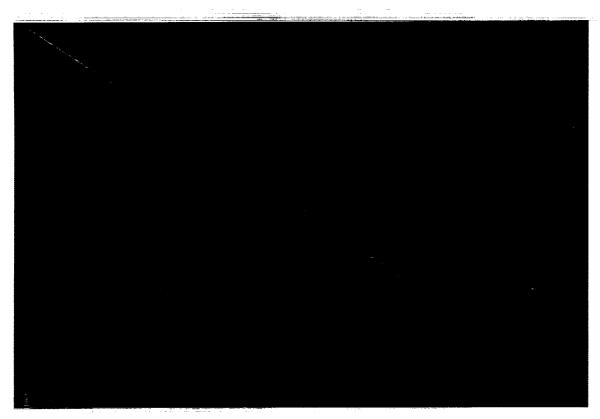
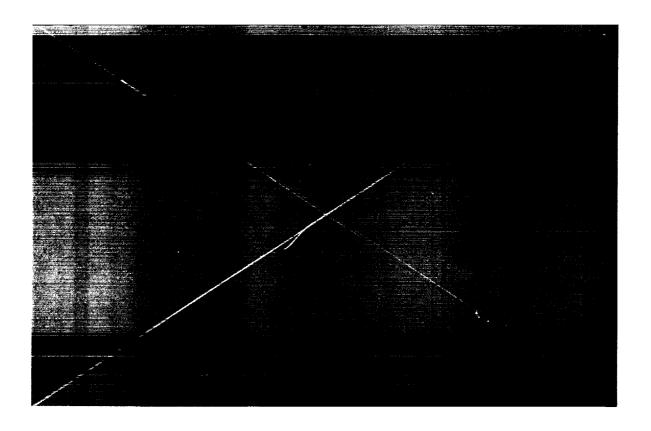


Figure 13. AKZO 463-6-3 primer on 2219-T87 aluminum after 90 days exposure to 5-percent NaCl salt fog.



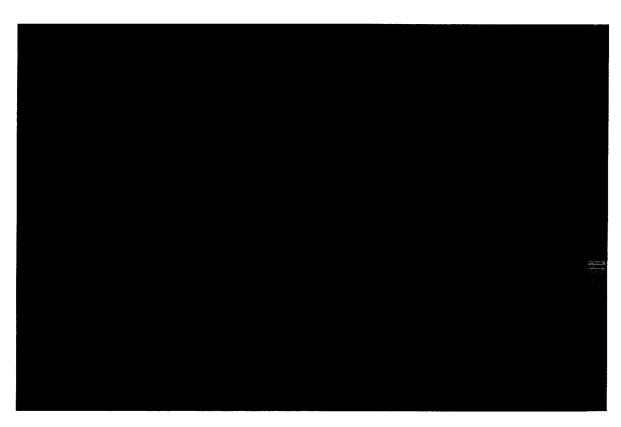
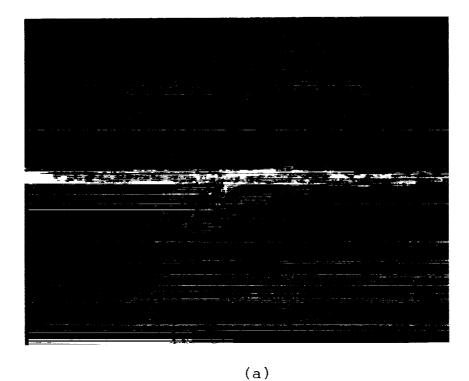


Figure 14. AKZO 463-6-78 primer on 2219-T87 aluminum after 90 days exposure to 5-percent NaCl salt fog.



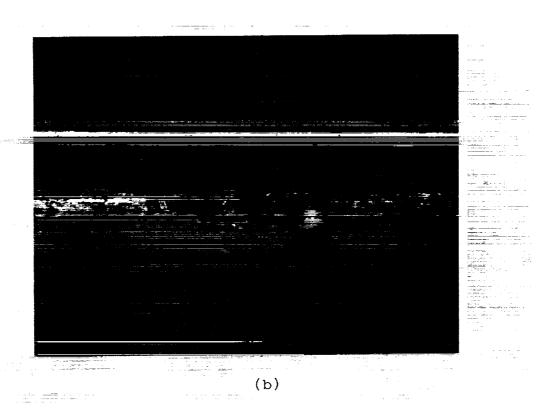
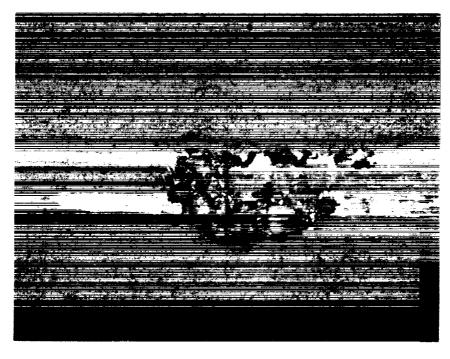


Figure 15. Pitting of (a) AKZO 463-6-3 and (b) AKZO 463-6-78 coated 7075-T73 aluminum after 90 days exposure to 3.5-percent NaCl alternate immersion (35X).



(a)

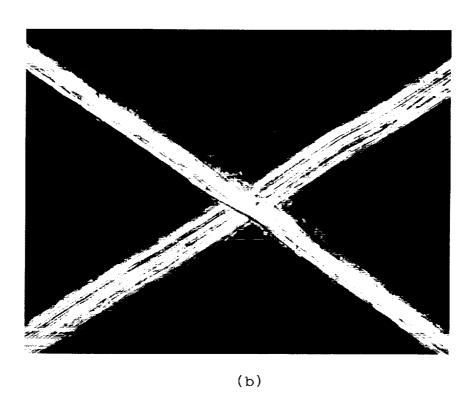
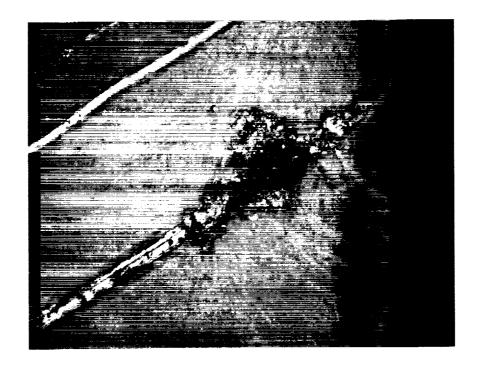
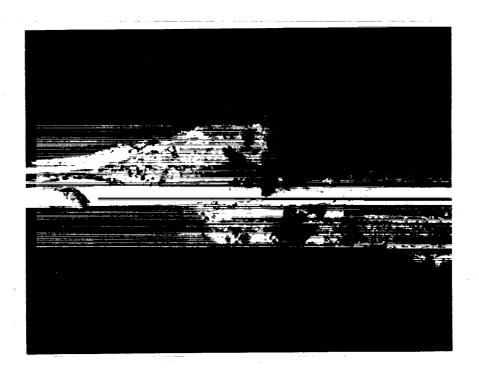


Figure 16. Pitting of (a) AKZO 463-6-3 and (b) AKZO 463-6-78 coated 7075-T73 aluminum after 90 days exposure to 5-percent NaCl salt fog (35X).



(a)

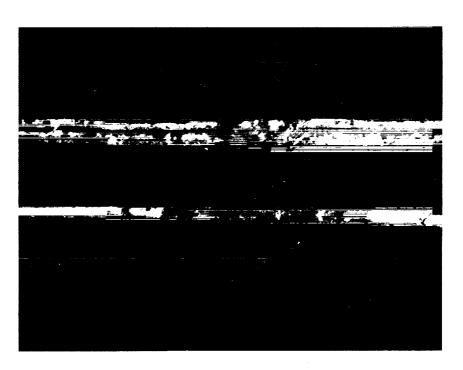


(b)

Figure 17. Pitting of (a) AKZO 463-6-3 and (b) AKZO 463-6-78 coated 2219-T87 aluminum after 90 days exposure to 3.5-percent NaCl alternate immersion (35X).



(a)



(b)

Figure 18. Pitting of (a) AKZO 463-6-3 and (b) AKZO 463-6-78 coated 2219-T87 aluminum after 90 days exposure to 5-percent NaCl salt fog (35X).

incorporated into the primer system. Since the 90-day alternate immersion and salt fog exposures showed no discernible difference between primers in terms of moisture resistance, a more sensitive method is required. The ac impedance technique is the only quantitative method available for the analysis of moisture resistant coatings.

WET TAPE ADHESION TESTING

Results of the 24-h immersion wet tape adhesion testing showed excellent adhesion for both primer systems. No evidence of adhesive failure was noted on any of the panels tested.

ELECTROCHEMICAL TESTING

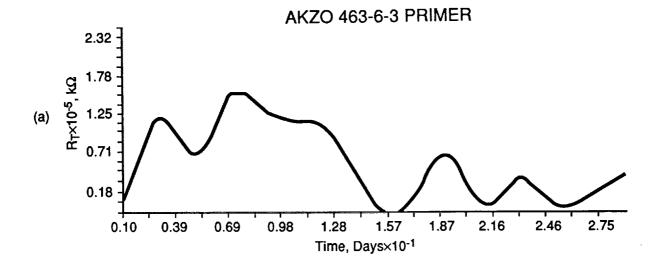
AKZO 463-6-3 Primer Coated 2219-T87 Aluminum

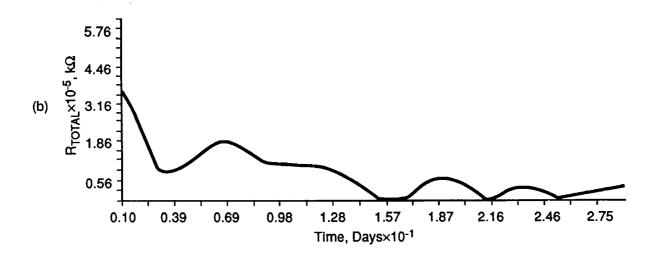
Alternating current impedance data for AKZO 463-6-3 primer coated 2219-T87 aluminum were analyzed using the equivalent circuit model in figure 2. Least-squares fit of the data over the 30-day exposure period resulted in eight time-dependent plots, one for each parameter in the model. In addition, the charge transfer (R_T) resistance, pore resistance (R_P) , and Faradic resistance (R_F) were combined as the total charge transfer resistance (R_{TOTAL}) . This value was used to calculate the corrosion current density (I_{CORR}) from the Stean-Geary Equation

$$I_{\text{CORR}} = \frac{ba \, bc}{2.303 \, (ba + bc)} \cdot \frac{1}{R_{\text{TOTAL}}} ,$$

using estimated Tafel constants (50 mV each for ba and bc).^{8–10} The 10 time dependent plots are shown in figures 19 through 22.

In general, the capacitances show trends of increasing with time, while the resistances are generally decreasing. From figure 19, it is apparent that the R_T (fig. 19a) controls R_{TOTAL} (fig. 19b) and therefore I_{CORR} (fig. 19c) starting on about the seventh day. Before this, R_{TOTAL} and I_{CORR} are controlled by R_P (fig. 21a) and R_F (fig. 21b). The large initial values of these parameters indicate this primer's excellent resistance to moisture. This is supported by low initial capacitance values (particularly the double layer capacitance at the metal-coating interface) and a low and relatively constant I_{CORR} through the first 10 days of immersion. After the 13th day, R_T , R_{TOTAL} , and I_{CORR} become cyclic in nature. This behavior in primer coated aluminum has been reported previously,⁷ and involves competition between two possible reaction mechanisms for aluminum corrosion. During the initial stages of immersion, the cell potential and corrosion mechanism are controlled by the oxygen reduction reaction. As the primer becomes "wetted" and oxygen rich electrolyte makes contact with the metal surface, an amorphous layer of Al₂O₃ forms. The thickness of this layer depends on the cell potential, which is a function of oxygen concentration ($E^{\circ}Cell = 2.06 + 0.0148 \log [O_2]$). As long as sufficient oxygen is available, this mechanism is dominant, and a relatively constant corrosion rate is observed. As the oxygen concentration at the metal-primer interface decreases, the cell potential drops, with concurrent thinning of the Al₂O₃ layer, and the hydrogen evolution reaction is favored (E°Cell = 0.832 V). The corrosion current for this reaction is greater (roughly an order of magnitude) than for the oxygen reduction reaction and an increase in I_{CORR} is observed. However, diffusion of aluminum through the thinner Al₂O₃ film is also accelerated and film growth proceeds, with a





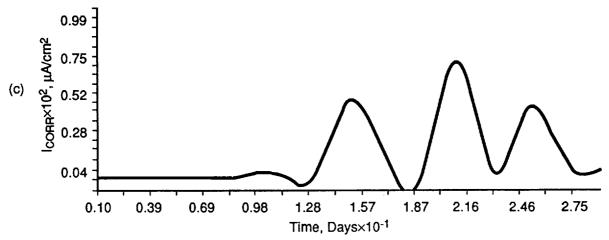
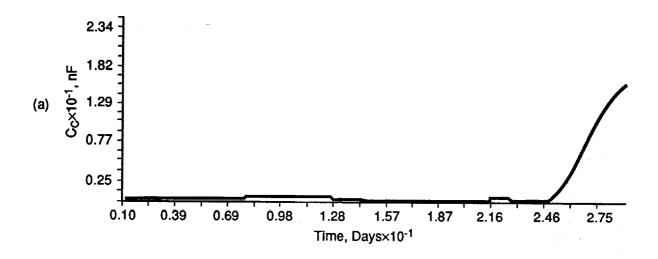


Figure 19. $R_{\rm T}$, $R_{\rm TOTAL}$, and $I_{\rm CORR}$ versus time—AKZO 463-6-3 primer coated 2219-T87 aluminum.

AKZO 463-6-3 PRIMER



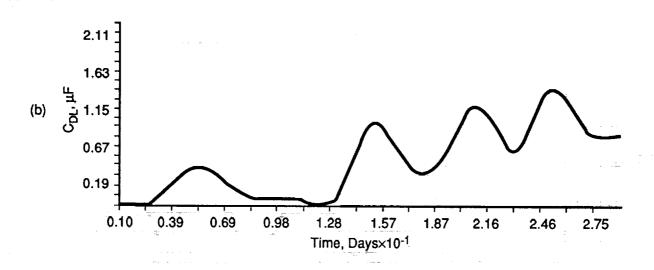
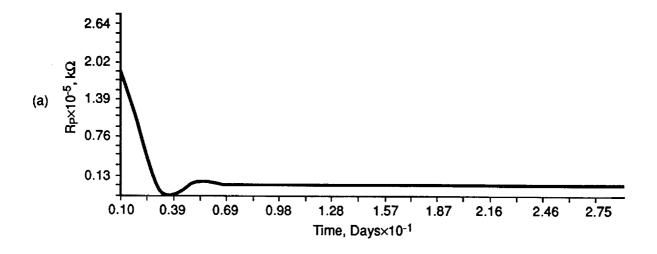


Figure 20. C_C and C_{DL} versus time—AKZO 463-6-3 primer coated 2219-T87 aluminum.

AKZO 463-6-3 PRIMER



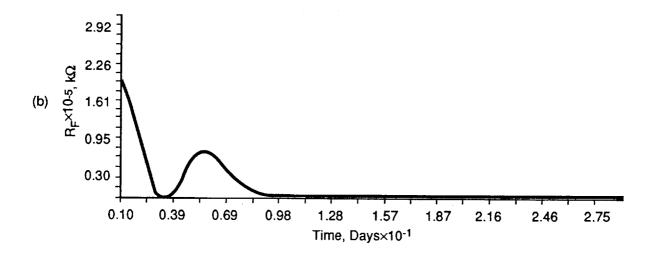
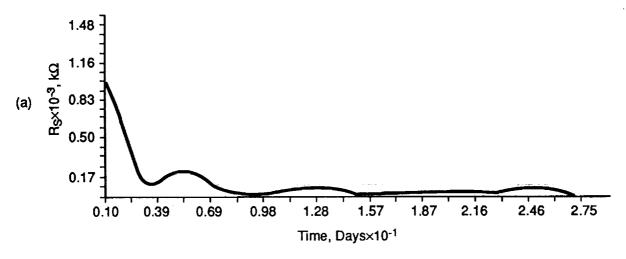
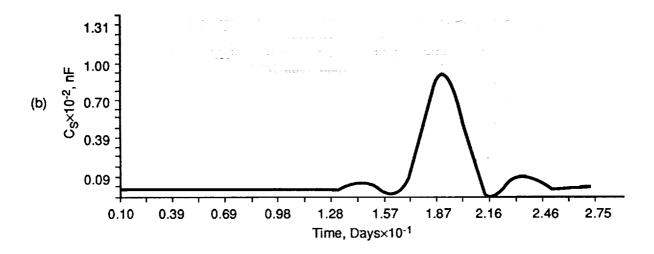
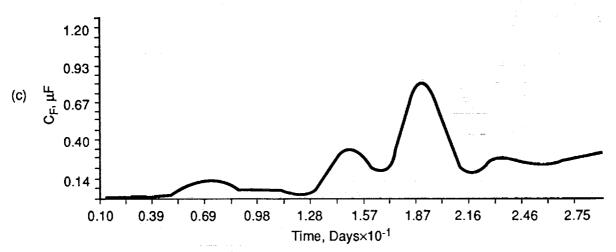


Figure 21. R_P and R_F versus time—AKZO 463-6-3 primer coated 2219-T87 aluminum.







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Figure 22. R_S , C_S , and C_F versus time—AKZO 463-6-3 primer coated 2219-T87 aluminum.

subsequent decrease in corrosion rate. Film thickness and oxygen concentration increase during this phase until the oxygen concentration reaches a level sufficient to favor the oxygen reduction reaction, and the cycle is repeated. The similarities between the $I_{\rm CORR}$ and the double layer capacitance (C_{DL}) (fig. 20b) curves, especially after 13 days of exposure, further illustrate that the controlling mechanism in this system is charge transfer at the metal-primer interface, and give credence to the theory that the corrosion current depends on the thickness of the Al_2O_3 barrier layer. As the barrier thickness decreases due to decreasing oxygen concentration, the cell potential drops and the capacitance at the metal surface increases; therefore, an increase in C_{DL} (fig. 20) is observed. Concurrently, a thinner barrier allows more current to pass, and therefore, an increase in corrosion current is also noted.

Other parameters in the equivalent circuit model contribute to the overall impedance, but their effect is overshadowed. For example, the sharp increase in the coating capacitance (C_C) (fig. 20a) after 25 days gives an indication of coating breakdown and in primer coated steels correlates well with an increase in I_{CORR} . However, in this system, there is no correlation between the increase in C_C and I_{CORR} , and I_{CORR} is actually decreasing during this time. Therefore, even if this increase in C_C is due to coating deterioration, the effect on the overall corrosion rate is insignificant compared to the rate controlling effects at the primer-substrate interface.

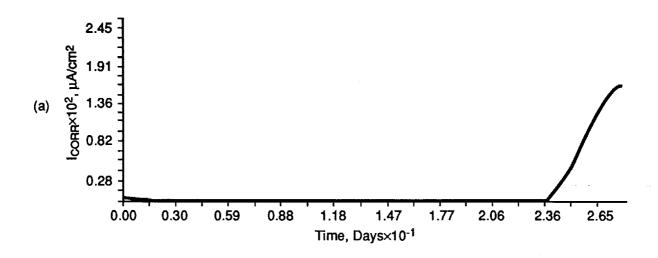
As stated previously, impedance runs were conducted every other day for 30 days, but samples remained in solution for 97 days. Two additional impedance scans were performed at 70 to 96 days, resulting in corrosion current densities of 0.00038 and $0.00030 \,\mu\text{A/cm}^2$, respectively, both of which are lower than the average current density during the first 30 days $(0.00122 \,\mu\text{A/cm}^2)$. While these values probably represent the low current density portion of a cycle, they do demonstrate the exceptional protection provided by this primer system.

AKZO 463-6-78 Primer Coated 2219-T87 Aluminum

Alternating current impedance data for AKZO 463-6-78 primer coated aluminum were analyzed in the same manner as the AKZO 463-6-3 coated aluminum. The 10 time dependent plots are shown in figures 23 through 26. From figures 23 and 24, it is apparent that R_T (fig. 24c) controls $R_{\rm TOTAL}$ (fig. 23b), and therefore $I_{\rm CORR}$ (fig. 23a), for the duration of the testing. However, the contribution of R_F (fig. 24a) during the first 20 days is significant. The $R_{\rm TOTAL}$ curve shows a small peak at 7 days, then decreases slowly during the first 24 days of immersion. After 24 days, $R_{\rm TOTAL}$ decreases rapidly. The corresponding $I_{\rm CORR}$ curve is nearly constant during the first 24 days, then increases sharply. This can be attributed to blistering of the primer and subsequent pitting of the base material (fig. 27). Figure 27a shows the blister in the electrode sample, and figure 27b shows the depth of pit penetration after 97 days exposure, which is estimated at 0.007 in.

Capacitance values in the equivalent circuit model correlated well with resistances and $I_{\rm CORR}$. All three coating system capacitances (C_{DL} , C_C , and C_F) (figs. 25b, 25a, and 26c) were relatively constant or slightly increasing during the first 24 days of immersion, followed by sharp increases. Corresponding resistances were nearly constant or slightly decreasing, followed by sharp decreases. Evidence of primer system failure was observed in all parameters of the equivalent circuit (with the obvious exception of solution resistance and capacitance).

AKZO 463-6-78 PRIMER



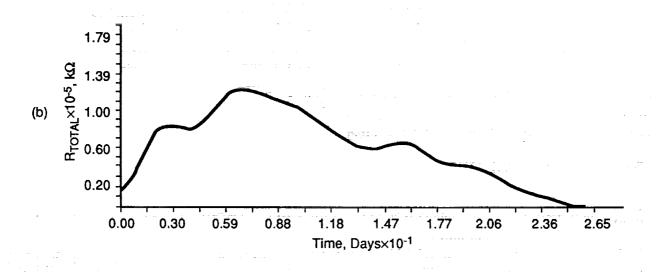
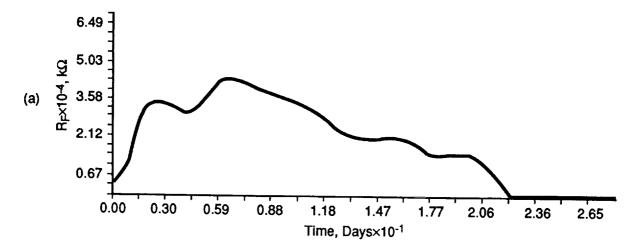
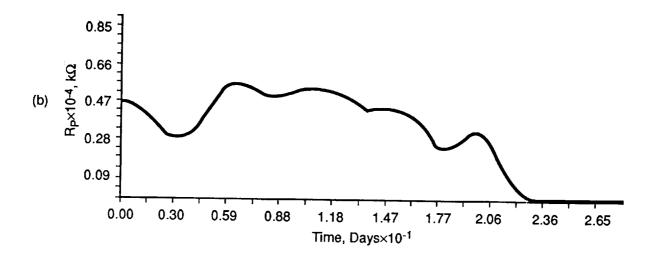


Figure 23. I_{CORR} and R_{TOTAL} versus time—AKZO 463-6-78 primer coated 2219-T87 aluminum.





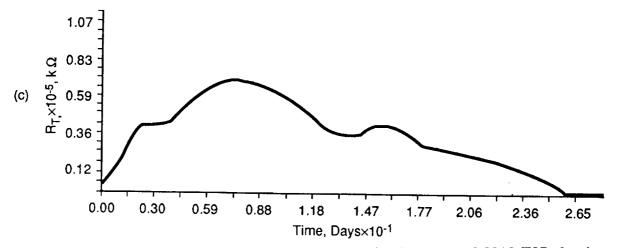
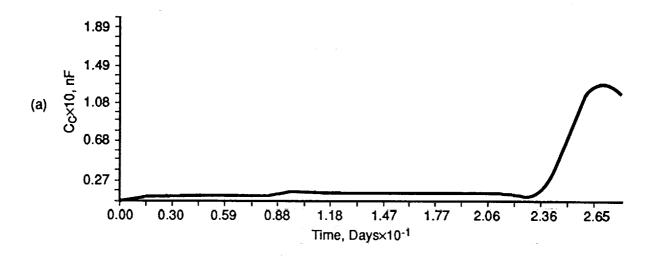


Figure 24. R_F , R_P , and R_T versus time—AKZO 463-6-78 primer coated 2219-T87 aluminum.

AKZO 463-6-78 PRIMER



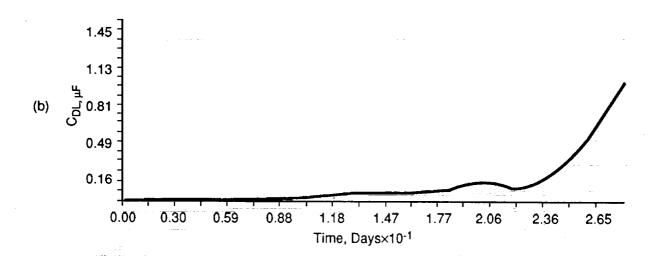
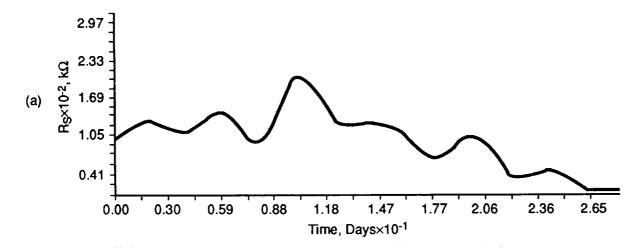
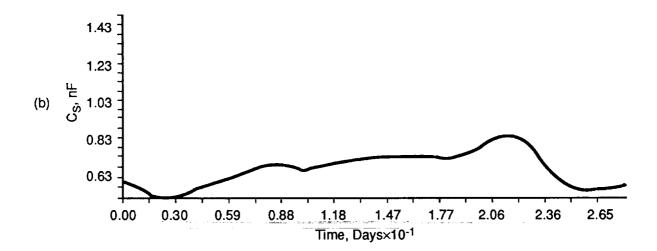


Figure 25. C_C and C_{DL} versus time—AKZO 463-6-78 primer coated 2219-T87 aluminum.





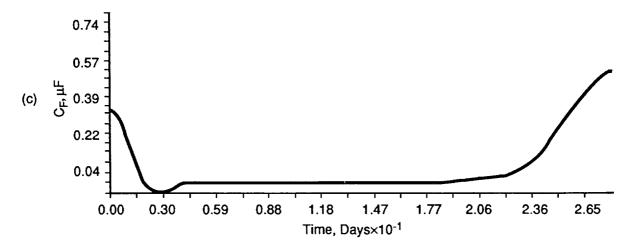
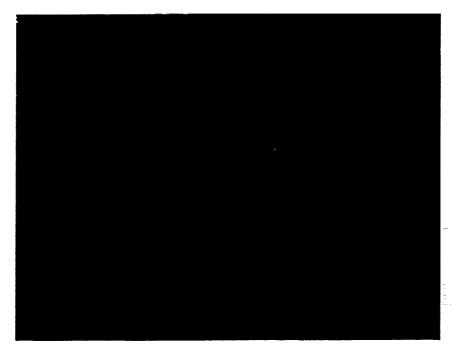


Figure 26. R_S , C_S , and C_F versus time—AKZO 463-6-78 primer coated 2219-T87 aluminum.



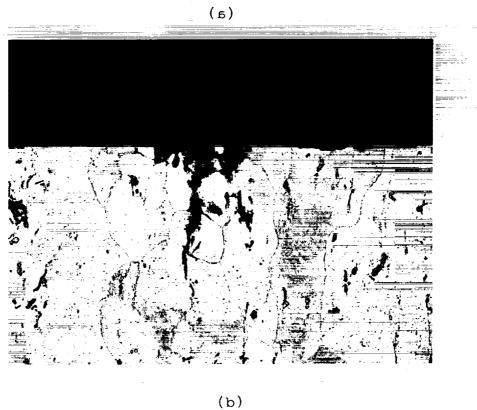


Figure 27. (a) Blistering of AKZO 463-6-78 primer on 2219-T87 aluminum electrode sample (25X) and (b) depth of pit penetration in 2219-T87 electrode sample (200X).

Data taken after the 1-month test at 71 and 97 days indicated accelerated corrosion current $(0.044~\mu\text{A/cm}^2\text{ and }0.058~\mu\text{A/cm}^2\text{ for }71\text{ and }97\text{ days, respectively})$. These currents were large enough to utilize the less sensitive direct current method for comparison. Direct current polarization resistance measurements resulted in current densities of $0.011~\mu\text{A/cm}^2$ and $0.013~\mu\text{A/cm}^2$ at 71 and 97 days, respectively, in good agreement with the ac impedance method of corrosion current estimation.

The cyclic nature observed in the $I_{\rm CORR}$ curves for the AKZO 463-6-3 coated aluminum was not seen in this system. This can be explained by the self-propagating nature of pitting corrosion. The large pit which formed subsequent to primer failure precluded the natural healing of anodic sites associated with the cyclic mechanism. After pit initiation, dissolution of aluminum metal within the pit produced an excess positive charge in this area, resulting in migration of chloride ions to maintain electroneutrality. Hydrolysis of the metal chlorides resulted in a high concentration of hydrogen ions, which increased the corrosion rate within the pit. Since oxygen diffusion into the pit was limited, surfaces adjacent to the pit provided sites for the oxygen reduction reaction, and were therefore protected from metal dissolution. This entire process accelerated with time and completely dominated the corrosion current. This explains the two orders of magnitude difference in corrosion current between the primer coated electrode samples after 97 days immersion (0.058 μ A/cm² for the 463-6-78 primer and 0.0003 μ A/cm² for the 463-6-3 primer).

CONCLUSIONS

This work has compared the performance of two epoxy primers using conventional and electrochemical methods. The conventional corrosion media, 3.5-percent NaCl alternate immersion and 5-percent NaCl salt fog, indicate that the new, low VOC primer (AKZO 463-6-78) performs better than the current primer (AKZO 463-6-3) with respect to corrosion protection. Evidence of this was shown by the lower frequency and severity of pitting in the scribe marks of exposed panels. The improved corrosion protection is attributed to a higher concentration of more effective inhibitor additions in the 463-6-78 primer (10 to 25 percent strontium chromate versus <10-percent calcium and lead chromates). No discernible difference between the primers was noted in areas away from the scribe, even after 90 days exposure to alternate immersion and salt fog, indicating exceptional resistance provided by both primers to SRB environments.

The electrochemical impedance testing showed definite differences between the two primers in 3.5-percent NaCl, and was effective in supplying quantitative data for comparison. Data for the AKZO 463-6-3 primer indicated no change in initial coating resistance or corrosion current during the first 13 days of immersion. After 13 days, the corrosion current became cyclic in nature, with a relatively low average rate during the remainder of the immersion period. No blistering of the primer nor pitting of the substrate was noted, even after 97 days immersion.

Data for the AKZO 463-6-78 primer showed little change in initial coating resistance and corrosion current through the first 20 days. After 20 days, however, blistering of the primer and pitting of the substrate resulted in an accelerated corrosion rate. The corrosion rate at the end of the 30-day immersion period was an order of magnitude greater than the 30-day average for the 463-6-3 primer. At 97 days, this difference was two orders of magnitude.

This apparent conflict in results may be explained as follows. The conventional testing is intended to simulate actual hardware environments, but does not include total immersion testing. Even 90 days of alternate immersion is actually only 15 days in solution. From the electrochemical data, it is apparent that both systems can easily tolerate 15 days of immersion with little or no change in the initial coating condition. For this reason, no difference between primers was noted away from the scribe after alternate immersion and salt fog exposure, and the 463-6-78 primer performed better due to its inhibitor additions. Differences between primers based on electrochemical data were not manifest until the last several days of the 1-month test period, and were the result of blistering on the 463-6-78 primer. This localized failure caused an increase in the corrosion current. which dominated the response for the sample, indicating superior performance by the 463-6-3 primer. However, it should be noted that the 463-6-78 primer held its initial resistance through the first 20 days (compared to 13 days for the 463-6-3 primer) of immersion in the 3.5-percent NaCl solution. In addition, the current electrode sample size is only 1 cm². Since the frequency of paint blistering, pitting corrosion, and like processes are based on statistical probability, the area of the sample is critical. Had larger panels been used on the electrochemical evaluation, it is possible that both primers would have blistered, giving comparable results. This hypothesis will be the subject of a future study, to be performed when a larger sample holder, now on order, becomes available.

RECOMMENDATIONS

Based on the results of this investigation, it is recommended that AKZO 463-6-78 primer be considered as a suitable alternative to the current AKZO 463-6-3 primer. It is emphasized that this work did not include compatibility with sealants or insulation. Therefore, this primer should be approved in applications for corrosion protection only, such as the bootstrap reservoir, until such studies are completed. In addition, while the 463-6-78 primer is VOC compliant, it also has increased levels of chromates and chlorofluorocarbons. Therefore, its use may be restricted in the future as acceptable levels of these contaminates are constantly being reduced by environmental legislation. The need for an environmentally safe, cost-effective form of corrosion protection for the space transportation system is of paramount importance.

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APPROVAL

AN EVALUATION OF CORROSION PROTECTION BY TWO EPOXY PRIMERS ON 2219-T87 AND 7075-T73 ALUMINUM

By Mitchell J. Mendrek

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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